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Rapid determination of quartz and structural characterisation of feldspars in rocks using FTIR

V Ramasamy*, K Anandalakshmi and V Ponnusamy

Department of Physics, Annamalai University, Annamalainagar-608 002, Tamil Nadu, India

E-mail : srsaraam@rediffmail.com

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Abstract : An infrared absorption method has been used to identify components (minerals) of rocks collected from various areas of Tamil Nadu without pre-treatments other than air drying and grinding and consequently with no significant modification of constitution that may occur with other conventional methods of examination requiring extensive pre treatments. The results obtained from the IR absorption spectra show the presence of quartz, feldspars, gibbsite, illite, maghemite, magnetite, hematite, kaolinite, vermiculite and palygorskite minerals. The quality of the quartz mineral is substantiated by calculating the crystallinity index. The relative distribution of quartz among the various sites are determined using extinction coefficient of the characteristic peak at 780 cm^{-1}. The quartz present in the samples from the site number 7 is in relatively well crystalline form than others. The presence of sanidine feldspars offers information on the temperature and pressure during the formation of rock resulting in Al/Si disorder.

Keywords : FTIR, mineral indentification, quartz and feldspars.

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1. Introduction

The Fourier transform infrared (FTIR) absorption spectra of rocks contain information about the mineralogy of the rock. Silica forms basic mineral for all types of rocks. The knowledge of mineral composition of silicate rock is very important in quartz processing. Crystalline silica is one of the most abundant component of the rock samples both in natural and industrial environment. In the field of rock mineralogy, study of infrared absorption spectra has made a remarkable progress, as exemplified by numerous research works on the absorptions in the Si-O region, on relationship between the chemical composition and the variation of position of absorption bands. Concerning the Si-O region a large number of research works have been carried out particularly on absorption of silica minerals [1,2].

The interest in the application of infrared spectroscopy to the study of inorganic compounds has been illustrated by Hunt *et al* [3]. The vibrational assignments and structural correlation have also been reported in the studies of silicates minerals by Roy and Frances [4].

In the present study, pure and various silicates were undertaken to provide some background information necessary for the interpretation of the infrared spectra of various rock samples.

2. Materials and methods

The present investigation deals with the infrared spectral analysis of some quartz contained samples of various areas of Tamil Nadu (South India). The samples used for the present study along with their location are as follows. Site No. 1: quartz with fissures (Jalakandapuram, Salem district). Site No. 2: white quartz (Taramangalam, Salem district). Site No. 3: rose quartz (Vellakoil, Erode district), Site No. 4: semitransparent quartz (Tarapuram, Karur district), Site No. 5: quartz with amygdule (Vallam, Tanjavur district), Site No. 6, 8 and 12: pegmatite with quartz and feldspar (Manaparai, Trichi district), Site No. 7: quartz (Omallur, Salem district), Site No. 9: plagioclase feldspars (Ottanchatharam, Trichi district), Site No. 10: quartz with agate (Idappadi, Erode district), Site No. 11: gray with white quartz (Aravakkurichi,

* Corresponding Author

Karur district), Site No. 13: white quartz with iron impurities (Kanjamalai, Salem district), Site No.14-18: granitic samples (Thiruvannamalai, Pallavaram, Dindivanam, Ulundurpet and Perambalur), Site No. 19 and 20: sandy quartz (Chidambaram, Cuddalore district). The samples 1-5 contains 80 to 90% of quartz, samples 6-13 are feldspathic rock and the quartz were separated using hand picking in the usual manner. The samples 14-18 are granitic rocks and the quartz and other minerals were studied as and when required. Samples 19 and 20 are sandy quartz and the quartz were separated using hand picking.

According to Wadia [5], Saravanan [6], Pichamuthu [7] and Nagvi and Rogers [8], the rocks in the above area are having the minerals like quartz, feldspars (orthoclase, microcline, sanidine and albite), magnetite and kaolinite and are of crystalline nature, forms a part of the great Achaean complex of the peninsular India. All the rocks are coarse-textured and possess evidences of deep-seated metamorphism under conditions of high pressure and temperature.

The major and minor minerals were qualitatively determined using FTIR technique. The Nicolate avator 360 series FTIR spectrophotometer has been used of in the present work for recording the FTIR spectra of the samples at room temperature. The KBr pellet technique (1 : 20) was followed for handling rock samples for infrared analysis. For each area three samples were collected and for each sample, three pellet specimens were prepared and spectra were taken in the region 4000 to 400 cm^{-1}. The spectra containing more absorption peaks in the region 1500 to 400 cm^{-1} are considered for analysis as no useful information is obtained in the other regions. Some of the representative spectra are given in Figure 1.

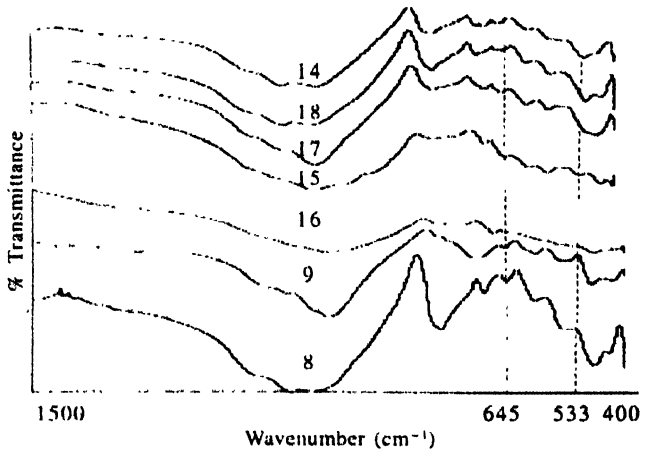

Figure 1. FTIR spectra of the site numbers 8, 9&14—18.

3. Results and discussion

From the FTIR spectra of all 20 samples, the IR absorption frequencies are observed in wavenumbers and are reported in Table 1. Comparing these observed frequencies with those available in literature [1-4,9-12], the minerals such as quartz, feldspars in different composition, gibbsite, illite, hematite, maghemite, megnetite, kaolinite, vermiculite and palygorskite are identified and are tabulated in Table 1

Table 1. Observed absorption frequencies (cm^{-1}) from FTIR spectra of samples from the various sites given in mineralwise

Sl. No.	Observed frequency cm^{-1}	Site number	Mineral name
1.	402–408	5, 15 & 16	Gibbsite
2.	415	2	Palygorskite
3	424	8 & 9	Maghemite
4.	426–436	14–18	Kaolinite
5.	458–464	1–20	Quartz
6.	499–506	5 & 16	Gibbsite
7.	512	1, 6 & 14	Palygorskite
8.	517	1–3, 10–12, 19 & 20	Gibbsite
9.	528	4 & 13	Illite
10.	533–543	7–9 & 14–18	Orthoclase
11.	580–584	8,9 & 14–18	Microcline
12.	629–650	8,9 & 14–20	Orthoclase
13.	661–666	12 & 13	Gibbsite
14.	671–674	2,5, 11 & 14–20	Maghemite
15.	687–692	1–20	Quartz
16.	716	9	Maghemite
17.	728–730	14–16 & 18	Illite
18.	775–780	1–20	Quartz
19.	799–804	1–14, 19 & 20	Quartz
20.	886	15	Hematite
21.	913	7	Palygorskite
22.	916	7	Gibbsite
23.	953	15	Magnetite
24.	958	16	Magnetite
25.	1004–1006	7 & 9	Vermiculite
26.	1013–1020	5–19	Albite
27.	1024–1026	1 & 2	Illite
28.	1045	8	Hematite
29.	1080–1083	1–20	Quartz
30.	1106	15	Magnetite
31.	1142	11	Albite
32.	1172–1175	1–20	Quartz
33.	1444–1449	5,7,8,9,11 & 13–20	Albite

3.1 Quartz:

Among all minerals, quartz (SiO_2) is invariably present in all samples with maximum proportion. The pattern of absorption in quartz can be explained by ascribing the 464 cm^{-1} region (Si-O asymmetrical bending vibrations), the bands in the region 690 cm^{-1} (Si–O symmetrical bending vibrations), the bands in the region 780 and 800 cm^{-1} (Si-O symmetrical stretching vibrations), while the 1080 and 1175 cm^{-1} absorption region arises from Si-O asymmetrical stretching vibrations due to low Al for Si substitution.

This assignment is in good agreement with the observation on the quartz minerals obtained by Hlavay *et al* [1]

3.2 Crystallinity index :

When crystallinity is minimum, the minerals are said to be in disordered state and when it is maximum, the minerals are considered to be in ordered state. The crystallinity of quartz will give a clear indication on the crystalline forms of other minerals because quartz is the mineral which crystallizes last. If this crystallinity is maximum then the other minerals are also expected to be equally well crystallized. Hence, it is useful to find out the crystallinity of quartz rather than for other minerals.

The intensity of the absorption band [13] at 695 cm^{-1} is due to the vibrations in octahedral site symmetry and at 780 cm^{-1} is due to the vibrations in tetrahedral site symmetry. The tetrahedral symmetry is stronger than the octahedral symmetry. If any structural change taking place, the damage occurs first in octahedral then in tetrahedral symmetry [14]. Therefore, the intensity of the bands due to the vibrations in these two symmetries, will supply an direct information on the crystallinity. Following Hlavay *et al* [1], the crystallinity index are computed by taking the absorption intensity ratios between the bands at 778 cm^{-1} and 695 cm^{-1} and are reported in Table 2 for all the samples by constructing the tangent base line for these bands. The values are drawn with respective to the site numbers and are shown in Figure 2. From this, it is observed that the degree of crystallinity decreases, the 695 cm^{-1} peak intensity decreases considerably and the ratio between I778/I695 cm^{-1} increases (crystallinity index increases). It is found that the sample number 8 and 18 having the values 3.43 and 3.62 respectively, show low degree of crystalline quartz, samples numbers 3, 6, 9, 11, 14, 16, 19 and 20 having the values 2.66 to 2.00, show intermediate crystalline structure and the remaining samples having the values 1.94 to 1.59, show high crystalline structure. Any significant change in the crystallinity index can be attributed to the geological conditions of formation like, transport or deposition or by mechanical treatment such as grinding [2,11] As seen from the Figure 2, the index varies from 1.59 to 3.62. This variation may be due to the minerals which are formed at different geological conditions. In the present study, it is observed that there is a slight shift in the characteristic doublet peaks (780 cm^{-1} and 800 cm^{-1}). The reason for this slight variation may be due to any impurities or crystal defects or isomorphous substitution [15].

Table 2. Crstallinity index of quartz and extinction coefficient (K) of quartz for the peak at around 778 cm^{-1}.

Site Number	No. of samples analysed	Average I777 / I695	Crystallinity Index	Standard deviation	$K=\frac{D\Delta}{m}$
1	3	4.4/2 3	1.91	0 002	86 34
2	3	2.4/1.4	1.71	0 003	40 70
3	3	6.4/2.9	2.21	0.002	159 73
4	3	4.0/2.2	1.82	0.003	76.47
5	3	2 8/1.5	1 87	0 001	50.45
6	3	4 0/1.6	2 50	0.002	70.31
7	3	6.2/3.9	1.59	0.002	135.69
8	3	5.5/1.6	3 43	0 003	106.08
9	3	1 6/0.6	2 66	0.003	1 54
10	3	4 2/2 2	1.91	0 003	77 03
11	3	3.8/1.8	2.11	0.001	70 06
12	3	3.1/1.6	1.94	0 002	51 81
13	3	4.6/2.5	1.84	0.001	96.82
14	3	1.8/0.7	2.57	0.002	28.37
15	3	0.5/0.3	1.67	0.002	3.82
16	3	0.7/0.3	2.33	0.001	3.52
17	3	1.5/0.8	1 88	0.003	25.65
18	3	2.9/0.8	3.62	0.003	49 40
19	3	3.4/1.7	2.00	0 002	58.59
20	3	4.2/2.0	2 10	0 002	71.72

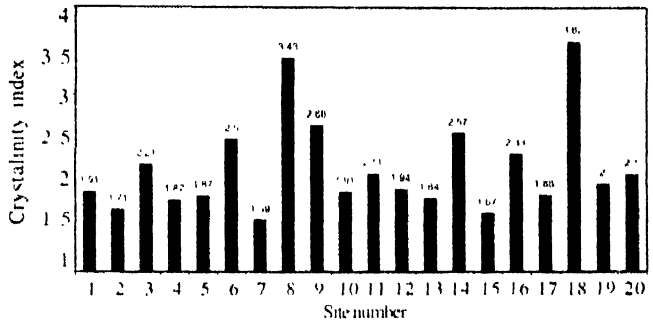

Figure 2. Crystallinity index of quartz for various sites

In any natural mineral, bending vibration modes could give more useful information on the nature of mineral with regard to the structural stability. The symmetrical bending vibrations of Si–O group obtained at 695 cm^{-1} is determinative of quartz, whether it is crystalline or amorphous. In the amorphous state, 695 cm^{-1} will be missing. This is a well known fact [1]. In the present study, 695 cm^{-1} peak is present in the spectra of all the sites ; therefore the quartz mineral in all the samples are in crystallised form.

Among the 20 samples analysed, the sample number 7 is supposed to contain well-crystallised form of quartz and the sample number 18 is considered to have poorly crystalline form of quartz *i.e.*, the quartz in sample number 18 may be associated with impurities during the crystallisation. Therefore it is true for the quartz in granite.

3.3 Feldspars

For the sample numbers 1-4, the feldspar peaks are not observed. From the Table 1, the peaks pertaining the range 533-543 cm^{-1} due to Si-O asymmetrical bending vibrations, 580-584 cm^{-1} due to O-Si(Al)-O symmetrical bending vibrations, 629–650 cm^{-1} due to Al-O coordination vibrations, 1013-1020 cm^{-1} due to Si(Al)-O symmetrical stretch-

ing vibrations, and 1444-1449 cm^{-1} asymmetrical stretching vibrations are observed, which match very well with the results of earlier workers [2,3,16,17].

The feldspar group of minerals are of several types such as orthoclase, microcline and sanidine (K-Feldspars), albite (Na-Feldspar) and anorthite (Ca-Feldspar). Though three feldspars (orthoclase, microcline and sanidine) are having same chemical formula ($KAlSi_3O_8$), they differ in structure (orthoclase-monoclinic, microcline-triclnic and sanidine-tetrahedral).

To quantify the varying degrees of disorder possible in K-Feldspars, the results obtained by Laves and Hafner [16] and Bahat [17] for a number of terrestrial samples of three possible polymorphs (orthoclase, microcline and sanidine) will be very useful in the present study. They found that two peaks at around 642 cm^{-1} (say band A) and 529 cm^{-1} (say band B) were very much sensitive to structural changes, as noticed from the decrease of the band A (642-632 cm^{-1})and an increase of the band B (529-543cm^{-1}) in going from microcline to orthoclase to sanidine.

In the present study, the frequency difference between the band A (650-629 cm^{-1}) and band B (533-543 cm^{-1}) can be taken into account in identifying the form of feldspar present. The frequency difference between these two bands can be used as an indication of relative degree of disorder

Table 3. Estimation of feldspar class by observing the frequency difference between two bands.

Sample number	Position		Frequency difference	Feldspar class
	Band A (cm^{-1})	Band B (cm^{-1})		
16	650	543	107	Orthoclase
9	648	533	115	Microcline
8	645	533	112	Microcline
14	643	543	100	Orhoclase
18	638	532	106	Orhoclase
17	638	538	100	Orhoclase
15	629	537	92	Sanidine

in the feldspar lattice. Studies on the terrestrial samples [16,17] showed that the frequency difference decreased from 115 to 100 to 92 cm^{-1} in going from microline to orthoclase to sanidine respectively. By considering the above suggestions, the frequency difference between these two bands are found out and are given in Table 3.

From this, it is observed that for the samples from site number 9 and 8, the largest frequency difference of 115 and 112 cm^{-1} suggest the presence of microcline and for the remaining samples 14, 16, 17 and 18, a medium frequency difference between 107 to 100 cm^{-1} indicates the orthoclase type. In the sample 15, a lowest frequency difference of 92 cm^{-1} is attributed to sanidine type. The remaining samples are not having these two peaks. In sample 7, the peak at 538 cm^{-1} and in sample 19 and 20, 645 cm^{-1} peak alone is observed. The studies on terrestrial samples [16,17] also showed that the thermal impact will result in Al/Si ordering of these feldspars which in turn may be correlated with the frequency difference of absorption bands. In the present work, the largest frequency difference of the samples 9 and 8 is an indication of higher degree of Al/Si order and the samples 14, 16, 17 and 18 are medium degree of Al/Si order. The sample number 15 is having the lowest degree of Al/Si order. The reason for the lowest degree of Al/Si order is due to higher temperature during the formation of the rock [17].

The peak in the range of 533-543 cm^{-1} is due to Si O asymmetrical bending vibrations and at 629-650 cm^{-1} is due to Al-O coordination vibrations, indicate the presence of orthoclase and at 580-584 cm^{-1} is due to O-Si(Al)-O bending vibrations for microcline. According to Laves and Hafner [16] and Bahat [17], the peaks appearing at around 1444 cm^{-1}, 1013 cm^{-1} and 1142 cm^{-1} indicate albite (Ca low), another form of feldspars, is also present along with microcline and orthoclase.

The peak centered at 1013-1020 cm^{-1} observed for all the samples except 1-4 and 20, may be due to the increase of Ca ions replacing Na ions in the structure of albite. The albite ($NaAlSi_3O_8$) and anorthite ($CaAl_2Si_2O_8$) are completely miscible and together form an isomorphous series ranging from soda feldspar at one end to the pure lime feldspars at the other end. In albite-anorthite series, more and more Ca ions can be isomorphically substituted [18,19]. If these Na ions are completely removed then the formation of anorthite minerals ($CaAl_2Si_2O_8$) will take place and this albite will not show any absorption peak. The peaks at 577, 602, 622, 666, 683, 728, 757, 929, 986 and 1085 cm^{-1} correspond to the spectra of anorthite [20]. As the peaks pertaining to anorthite are not present in the spectra of the present samples, it may be opined that albite is not completely transformed into its end member (pure lime feldspar) and albite mineral is present in some samples containing only sodium and in other samples, the same mineral is contaminated with calcium.

According to Couty and Velde [21], the band around 1000 cm^{-1} region will develop if the pressure increases Since the appearance of new bands around 1013 cm^{-1} is seen in the samples one may conclude that the pressure during the magma formation might have been higher.

The bending vibrations at 580-584 cm^{-1} observed from the spectra of the samples 8, 9, 14, 15, 16, 17, and 18 are assigned to O-Si(Al)-O bonds. The variations of the band frequencies 580-584 cm^{-1} may be considered to be nearly

in the range of resolution of IR spectrophotometer. Another reason may be due to overlying burden causing pressure which changes the bond angle. If the bond angle varies, drastic changes in the bending mode frequencies may be expected to be present [21]. But there is no drastic change in frequency of this bending mode. Hence, an useful information can be obtained from the stretching vibration of O-Si(Al)-O bonds on the impact of pressure to large changes in frequencies, instead of bending vibrations.

The IR absorption spectra of fully ordered series will show strong signals with small line widths and every spectral feature will be well-resolved, whereas the disordered series may exhibit broad peaks resulting from random Al-Si distribution and varying amounts of alkali ions in the feldspar structure.

The variation of composition causes frequency shifts and changes in band intensities. The absorption spectra of the samples undertaken in the present investigation show the presence of feldspars of three types (Na, K, Ca) as evidenced from the existence of broad peak. The broadening of the peak is strong for Si-O stretching modes between 1200-1000 cm^{-1} [11]. Hence, the broad feature of the absorption band of feldspars at 1013-1020 cm^{-1} in the present work is always associated with the strong Si–O stretching vibrations.

3.4 Other minerals :

The other minerals are also identified using the view of earlier workers [9,10]. The IR absorption peak observed in the range 402-408 cm^{-1}, a peak between 499- 506 cm^{-1}, a peak at 517 cm^{-1}, a peak in the range 661-666 cm^{-1} and a peak at 916 cm^{-1} are the characteristic peaks of gibbsite mineral($Al_2O_3.3H_2O$). The presence of the peaks at 528 cm^{-1}, 728 cm^{-1}, 1024 cm^{-1} and 1026 cm^{-1} confirm the illite mineral ($(OH)_4$, $K_2(Si_6Al_2)Al_4O_{20}$). The absorption spectra of the present samples show the peak in the range 671-674 cm^{-1}, a peak at 716 cm^{-1} and at 424 cm^{-1}, which are the characteristics of maghemite ($MgFe_2O_4$). The peaks observed at 1045 cm^{-1} and 886 cm^{-1} show the presence of hematite (Fe_2O_3). The peaks observed at 953, 958 and 1106 cm^{-1} indicate the magnetite mineral (Fe_3O_4). The clay mineral kaolinite and mica mineral vermiculite $(KX_3(Si,Al)_4O_{10})(OH,F)_2$ are present due to presence of the peaks in the range 426-436cm^{-1} and 1004-1006 cm^{-1} respectively.

Palygorskite and sepiolite are the intermediate layer silicates between di-and tri-octahedral types respectively. But in the present study, palygorskite mineral alone is present in the samples 1, 2, 6, 7 and 14. The characteristic peaks observed for this minerals are 415, 512 and 913 cm^{-1}. But the sepiolite mineral is not present in these samples. The reason for the absence of this mineral is that the di-octahedral characteristics is dominent than the tri-octahedral, which is shown by the well-defined AlAlOH deformation band at 913 cm^{-1}.

Since the intensities of the peaks observed for above minerals are weak to medium, these minerals are considered as traces.

3.5 Relative distribution of quartz :

To quantify the relative distribution of quartz, the extinction coefficient for the characteristic peak at around 778 cm^{-1} has been calculated (Table 2) for all the 20 samples under investigation, using the relation $K=DA/m$, where k=extinction coefficient, D=optical density, A=area of the pellet and m=mass of the sample.

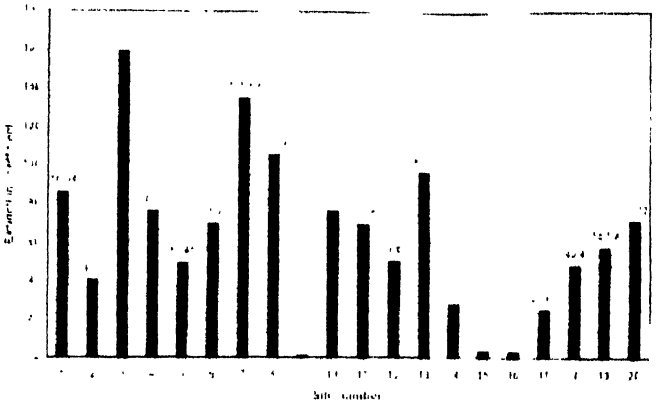

Figure 3. Extinction coefficient of quartz peak at around 778 cm^{-1} for various sites

A plot of site number *versus* extinction coefficient are drawn and shown in Figure 3. From this, it is observed that the sample number 3 is having a maximum extinction coefficient of 159.73. This site is taken as reference to have maximum quartz. The site number 9 is having a minimum extinction coefficient of 1.54. With these two as limits, the other sites may be arranged for the containment of quartz quantitatively in an order.

4. Conclusions

The infrared analysis of the various rock samples from different areas of Tamil Nadu indicates the presence of quartz, feldspars, gibbsite, illite, magnetite, maghemtite, hematite, vermiculite, kaolinite and palygorskite minerals.

Among the different minerals, quartz is present invariably in all the samples. Hence this mineral is considered to be a main or major constituent of the samples. Except the samples from site number, 1 to 4, the feldspar mineral is present in all the samples in different compositions *i.e.*, orthoclase, microcline, sanidine and albite. Hence this mineral is considered to be a minor mineral. All the other minerals are found to be as traces.

Two procedures were adopted for finding the crystalline nature of quartz. In the first method, the intensity ratio of the stretching mode (778 cm^{-1}) and bending mode (695 cm^{-1}) is calculated and results were interpreted. In the second method, the mere identification of the peak at 695 cm^{-1} is used for concluding the crystallinity of quartz. The study on the crystallinity index of quartz supplements the view that the conducive atmosphere was prevailing for the minerals to be in well crystallised state during the igneous rock formation at these sites. The presence of sanidine feldspars, confirms the higher temperature and pressure during the formation of rock resulting in Al/Si disorder.

The availability of quartz among the various sites was determined by comparing extinction coefficient of the samples. It is observed that the samples from site number 3 having maximum extinction coefficient, is having maximum quartz among all the sites but with lesser crystallinity. On the other hand, for the samples from the site number 7, quantity of the quartz is minimum but the crystallinity is maximum. Therefore the quality of the quartz from site from number 7 is higher than other sites.

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